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(NASA-CR-159553) X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF NICKEL AND NICKEL-BASE ALLOY SURFACE ALTERATIONS IN SIMULATED HOT CORROSION CONDITIONS WITH EMPHASIS ON EVENTUAL APPLICATION TO (Case Western

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X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF NICKEL AND
NICKEL-BASE ALLOY SURFACE ALTERATIONS IN SIMULATED HOT
CORROSION CONDITIONS WITH EMPHASIS ON EVENTUAL
APPLICATION TO TURBINE BLADE CORROSION

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SUMMARY

A study of the high temperature oxidation and Na_2SO_4 -induced hot corrosion of some nickel-base superalloys has been accomplished by using ESCA to determine the surface composition of the oxidized or corroded samples. Oxidation was carried out at 900 or 1000°C in slowly flowing O_2 for samples of B-1900, NASA-TRW VIA, 713C, and IN-738. Oxidation times ranged from 0.5 to 100 hr. Hot corrosion of B-1900 was induced by applying a coating of Na_2SO_4 to preoxidized samples, then heating to 900°C in slowly flowing O_2 . Corrosion times ranged from 5 min. to 29 hr. For oxidized samples, the predominant type of scale formed by each superalloy was readily determined, and a marked surface enrichment of Ti was found in each case. For corroded samples, the transfer of significant amounts of material from the oxide layer to the surface of the salt layer was observed to occur long before the onset of rapidly accelerating weight-gain. Some marked changes in surface composition were observed to coincide with the beginning of accelerating corrosion, the most striking of which were a tenfold decrease in the sulfur to sodium ratio and an increase in the Cr(VI) to Cr(III) ratio.

Goal of the Research

The goal of this research was to obtain information on the chemistry of the hot corrosion of nickel-base superalloys in simulated conditions with emphasis on eventual application to turbine blade corrosion. The novelty of our approach consisted of the use of new physical methods with firm potential to expand upon the knowledge gathered to date by studies which employed different methods. More detailed information was needed about the oxidation processes at the surface of the alloys. Moreover, it was very necessary to obtain as complete an image as possible of the qualitative and quantitative nature of the dynamic chemical processes occurring at different stages of corrosion. In other words, we wanted not only to identify all elements reaching the surface layers, but also to learn about their chemical state, which would then help us infer (at least in part) the mechanism of corrosion.

Means of the Research

In order to reach such a goal, we chose X-ray photoelectron spectroscopy (XPS or ESCA) as the main method of analysis. In ESCA (electron spectroscopy for chemical analysis):

- a) There is a net correlation between the measured electron binding energy and the oxidation state of the corresponding element.
- b) Measurements of all elements except hydrogen are possible.

- c) The information depth is very small, extending at most a few nanometers into the sample, thus allowing changes in composition at or near the gas-solid interface to be observed.
- d) Inert gas sputtering can be employed to expose deeper layers for analysis.

In a later stage, we also used ISS (ion scattering spectroscopy) and SIMS (secondary ion mass spectrometry), two methods of surface analysis that excellently complement ESCA. However, since these instruments became available only toward the end of our project, there was insufficient time to exploit them profitably. Nevertheless, even the results of the incipient work were showing clear promise. The samples we studied were provided and given oxidation and corrosion treatments by scientists at the NASA Lewis Research Center. The experimental methods are described in the appended manuscript, which has been submitted to the journal entitled "Oxidation of Metals."

Description of Results

The data obtained during the course of this study consist of a large number of X-ray induced photoelectron spectra from samples of unoxidized and oxidized superalloys B-1900, NASA-TRW VIA, 713C, and IN-738, and hot corroded B-1900, covering a wide range of oxidation or corrosion exposure times. With the help of additional spectra from unoxidized and oxidized pure metals and from related salts, the spectra from the superalloy samples were analyzed and interpreted to reveal extensive information about the chemical composition of the outer most few atomic layers of the samples. Despite the chemical complexity of the samples, all the

elements present (except H) at concentrations greater than a few parts per thousand were identified. In many cases spectral intensities were employed to compute approximate relative concentrations of the elements of interest. The peak positions (binding energies) and shapes allowed the oxidation states of the elements to be identified in most cases. Previous progress reports for this grant (see list below) contain many spectra, as well as tables of binding energies and of surface compositions. The appended manuscript includes much of the data in the progress reports, plus that from experiments conducted near the end of the grant period.

Our data revealed substantial migrations of specific elements occurring in the course of high temperature oxidation and Na_2SO_4 -induced hot corrosion. Specific observations and conclusions follow.

Conclusions

This work clearly demonstrates the usefulness of ESCA in the study of oxidation and corrosion of superalloys (and other complex materials) in spite of its semiquantitative nature. We will emphasize seven principle observations and conclusions of this work:

1. The surface of each of the "unoxidized" superalloy samples (which were machined to shape and cleaned with detergent, acetone, and alcohol prior to examination) was found to be significantly enriched in Al and Cr relative to the bulk. In each case, the percentage enrichment of Al exceeded that of Cr.
2. ESCA results for samples oxidized at 900 or 1000°C in slowly flowing O_2 showed clearly that B-1900 and NASA-TRW VIA are alumina formers and that the surface in

IN-738 is primarily TiO_2 . However, the surface composition of 713C oxidized at 900°C was found to change dramatically as a function of oxidation time, seeming to fit the alumina-former category after one hour but changing to the chromia-former category after longer periods of oxidation.

3. The surface of all the superalloy samples oxidized at high temperature was greatly enriched in Ti relative to the bulk. TiO_2 is the predominant surface phase on oxidized IN-738 and the second-most abundant on 713C. By contrast, the surface concentration of Ti did not exceed the bulk values (1-4%) for any of the "unoxidized" samples.
4. For preoxidized B-1900 samples exposed to just 30-45 minutes of Na_2SO_4 -induced hot corrosion, the total alloy element abundance at the surface ranged from 0.3 to 0.8 relative to Na. Thus, the transfer of significant amounts of material from the oxide layer to the surface of the salt layer begins long before the onset of rapidly accelerating weight-gain. A decrease in total alloy element abundance relative to Na was, however, observed after 6 hours of hot corrosion.
5. The ratio of Cr(VI) to Cr(III) was significantly greater after 6 hours of corrosion than at 4 hours. The atomic abundance of S relative to Na at the surface of Na_2SO_4 -coated B-1900 samples decreased an order of magnitude,

from 0.43 after 6 hours of hot corrosion to 0.04 after 8 hours. Among the alloy elements, Al and Ni increased in relative surface abundance and all the others decreased over the 6 to 8 hour period. Thermogravimetry showed that the onset of rapidly accelerating oxidation took place during this period.

6. For a B-1900 sample examined after 15 hours of Na_2SO_4 -induced hot corrosion, the surface abundances of Na, Ni, and Al were roughly equal, with Ni and Al accounting for two-thirds of the alloy element abundance. The oxide scale which remained attached after spontaneous spallation from a sample corroded for 29 hours was found to consist primarily of Mo and Ni. The spallation interface seems on the basis of stoichiometry, to be mostly $(\text{Ni},\text{Co})\text{MoO}_4$.
7. ESCA binding energies were interpreted to identify the chemical state of the alloy elements in oxidized and corroded samples. The results did not enable a distinction between the previously proposed mechanisms of Na_2SO_4 -induced hot corrosion.

Recommendations for Future Research

We expect surface analytical techniques such as ESCA to play an important role in the future study of the oxidation and corrosion of superalloys. To take greatest advantage of its surface sensitivity, we recommend that ESCA be used for careful examination of the earliest stages of oxidation or corrosion reactions. Use of an in situ reaction chamber

would allow much better control of the surface to be examined, and would facilitate the study of much finer variations in treatments. Scanning Auger Microprobe would also be very useful, since lateral inhomogeneity at the surface could then be observed.

Progress Reports Issued

1. First Semiannual Report (June-November, 1974), December, 1974.
NASA CR-140907.
2. Interim Report (December 1974-April 1975), May, 1975.
NASA CR-142899.
3. Second Semiannual Report (December, 1974-June, 1975), July, 1975.
NASA CR-143173.
4. Interim Report (July, 1975-December, 1976), January, 1977.
5. Third Semiannual Report (January-June, 1977), August, 1977.
NASA CR-154497.
6. Interim Report (July 1, 1977-November 19, 1977), November, 1977.

Oral Presentation

G.D. Mateescu, W.J. Carter, III, F.J. Kohl, C.A. Stearns, and G.C. Fryburg, "X-Ray Photoelectron Spectroscopy (ESCA) Study of Nickel and Nickel-Base Superalloy Surface Alterations in Simulated Hot Corrosion Conditions," 8th ACS Central Regional Meeting, Akron, Ohio, May 19-21, 1976.

Publication

S.R. Smith, W.J. Carter, III, G.D. Mateescu, F.J. Kohl, G.C. Fryburg, and C.A. Stearns, "ESCA Study of Oxidation and Hot Corrosion of Nickel-Base Superalloys," submitted to Oxidation of Metals.

APPENDIX I

ESCA STUDY OF OXIDATION AND
HOT CORROSION OF NICKEL-BASE SUPERALLOYS

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ABSTRACT

A study of the high temperature oxidation and Na_2SO_4 -induced hot corrosion of some nickel-base superalloys has been accomplished by using ESCA to determine the surface composition of the oxidized or corroded samples. Oxidation was carried out at 900 or 1000°C in slowly flowing O_2 for samples of B-1900, NASA-TRW VIA, 713C, and IN-738. Oxidation times ranged from 0.5 to 100 hr. Hot corrosion of B-1900 was induced by applying a coating of Na_2SO_4 to preoxidized samples, then heating to 900°C in slowly flowing O_2 . Corrosion times ranged from 5 min. to 29 hr. For oxidized samples, the predominant type of scale formed by each superalloy was readily determined, and a marked surface enrichment of Ti was found in each case. For corroded samples, the transfer of significant amounts of material from the oxide layer to the surface of the salt layer was observed to occur long before the onset of rapidly accelerating weight-gain. Some marked changes in surface composition were observed to coincide with the beginning of accelerating corrosion, the most striking of which were a tenfold decrease in the sulfur to sodium ratio and an increase in the Cr(VI) to Cr(III) ratio.

INTRODUCTION

The development of nickel-base superalloys is a continuing process, motivated primarily by the demand for materials with great strength and stability at ever higher temperatures for use in modern gas turbine engines. Improvement in high temperature strength has been sought, and achieved by increasing the aluminum and titanium content of nickel-base superalloys and consequently decreasing the chromium content (ref. 1). Although such developments have succeeded in permitting higher-temperature operation, a complex catastrophic oxidation process known as hot corrosion has become an important limiting factor (ref. 2). As a result, the hot corrosion of nickel-base superalloys is being thoroughly investigated in order to elucidate the reaction mechanisms and evaluate the roles of the various alloy components (ref. 3). The work reported here is part of such an investigation.

Over the past decade, x-ray photoelectron spectroscopy (also known as electron spectroscopy for chemical analysis - ESCA) has become a useful and widely applicable technique for the study of solid surfaces (ref. 4, 5). Its outstanding characteristics include: sensitivity to all elements except hydrogen; sensitivity to differences in chemical environment (enabling, for example, the identification of oxidation states); and surface sensitivity (due to photoelectron escape depths of just a few atomic layers). Some semi-quantitative information about the relative concentration of elements in the surface layer can be derived from the intensities of the spectral lines, although

the inherent uncertainties are rather large, especially for transition metals (refs. 6 & 7).

In recent years ESCA has been employed in many studies of alloy surface composition, oxidation, and corrosion (ref. 8). Such studies have been concerned with simpler, more homogeneous systems than the multi-element, multi-phase, nickel-base superalloys. Nevertheless, ESCA can yield useful results for complex systems; and it is complementary to the techniques commonly employed in studies of hot corrosion which include thermogravimetry, x-ray diffraction, electron microprobe, and microscopy.

We have studied by ESCA the oxidation of four commercial Ni-base superalloys: B-1900, NASA-TRW VIA, 713C, and IN-738. Samples of each were examined prior to high-temperature oxidation as well as after oxidation treatments at 900 and 1000°C in slowly flowing O₂. The hot corrosion of B-1900 was simulated by coating samples with Na₂SO₄, and then exposing them at 900°C to slowly flowing O₂. Many such samples were studied with hot-corrosion times ranging from 5 minutes to 29 hours.

To establish a data base for this study we recorded ESCA spectra for most of the elements contained in nickel-base superalloys, both as pure metals and as oxidized pure metals. These include Ni, Al, Co, Cr, Ti, Mo, Ta, W, and Nb. We also examined several salts of the alloy elements as well as Na₂SO₄ to facilitate the interpretation of spectra from oxidized or corroded superalloy samples.

EXPERIMENTAL PROCEDURES

All samples had a cylindrical shape consisting of two sections. The main body section was 19 mm high and 11 mm in diameter (except IN-738 which diameter was 5 mm). The upper section, 4 mm high by 2.5 mm in diameter was designed for insertion into the chuck of the spectrometer's sample holder. A 1.5 mm diameter hole through the upper section was provided so that the samples could be hung from a platinum wire hook in the oxidation and hot corrosion apparatus. The samples had a ground surface finish of eight microinches and were cleaned with detergent, acetone, and alcohol prior to use.

Oxidation and hot corrosion experiments with alloy samples were performed by hanging the samples in a 23 mm i.d. quartz tube contained within a vertical tube furnace. Oxygen, at atmospheric pressure, was flowed through the quartz tube at a rate of 100 cc/min. Oxidation time at 900° was varied over the range of 0.5 to 100 hours. Sample weight changes were continuously monitored with a recording microbalance. Single component pure metal samples were oxidized in still air in a muffle furnace and weight changes were not measured.

The corrosion treatment for each sample included the following: (a) preoxidation in oxygen for 100 hours at 900°C; (b) coating with Na₂SO₄ by spraying with a saturated aqueous solution of Na₂SO₄ to a specified weight per unit area coverage of dry Na₂SO₄; and (c) hot corrosion by heating the coated sample to 900°C in oxygen for a specified period of time. Specific corrosion treatments for individual B-1900 samples are

included in the Results and Discussion section.

All samples were examined with a Varian IEE-15 x-ray photoelectron spectrometer equipped with a high intensity magnesium anode ($K\alpha$ -radiation, 1253.6 eV). The operating parameters were: x-ray power, 640 W (8 kV, 80 mA); analyzer energy, 100 eV; channel width, 0.18 eV. The analyzer pressure was 10^{-6} - 10^{-7} torr, maintained by a turbomolecular pump and rotary foreline pump. In cases where sputtering was done, the approximate conditions were 5-10 minutes glow discharge at 1 to 2 kV and 2 to 4 mA in 40 to 50 millitorr Ar.

The binding energy of each photoelectron peak was taken to be the position of the peak maximum as determined by visual observation of a plotted spectrum. A DuPont 310 Curve Resolver was employed in cases of significantly overlapping peaks. The photoelectron binding energies were corrected for surface-charging effects by reference to the C 1s (hydrocarbon contamination) peak, which was assigned the standard binding energy of 285.0 eV. The width of this peak ranged from about 2.5 to 3.2 eV (FWHM). The estimated uncertainty of the binding energy ranged from ± 0.2 eV for simple intense peaks, to ± 0.5 eV for peaks that were complicated by multiplet splitting, multiple oxidation states, or overlap with less intense peaks of other elements. Some peaks were poorly defined due to very low intensity (low concentration of the element in the sample) and thus had even more uncertain binding energies.

For most samples, the series of spectra upon which the

semi-quantitative results are based was recorded in "sequential mode"; that is, the spectrometer scanned the region of the selected peak of each element in order of decreasing binding energy, then repeated this sequence until all the peaks were sufficiently well-defined. This minimizes the effect of any instrumental fluctuations on the relative intensities of the peaks. The area under each simple, symmetric peak was generally taken as the product of the peak height by the full width at half maximum. The area under each complex or poorly-defined peak was determined by square-counting, after the spectrum had been analyzed into individual components using the curve resolver. The background was assumed to be linear, or in some complex spectra, segmented.

The intensities thus determined were used to compute the approximate relative surface abundances of the elements in each sample. Three of the several factors (ref. 7) that enter into the relationship between observed intensity I_i and elemental concentration n_i were explicitly accounted for in these computations: the photoionization cross section σ , the spectrometer detection efficiency T , and the mean free path (of the photoelectron in the sample material) λ . The cross sections used were those calculated by Scofield (ref. 9). The relative effect of T was represented by its theoretical kinetic energy dependence (ref. 10), $T \sim 1/E$. The variation in λ was also approximated as a simple function of kinetic energy (ref. 6), $\lambda \sim E^{1/2}$. Thus, at this level of approximation, the relative surface concentration of two elements is given by n_1/n_2 , where

$n_i = I_i / (\sigma_i T \lambda) = I_i E_i^{1/2} / 2 \sigma_i$. The fraction of one alloy element relative to the total alloy surface abundance is given by $n_i / \sum n_i$, where the summation includes all the alloy elements.

There are several sources of uncertainty and error that affect the semi-quantitative results in this study. The most profound is the inhomogeneity of the superalloy sample surfaces. Because the surface area from which photoelectrons were obtained was large (roughly 4 cm²), the ESCA intensities reflect an average composition only.

The large number of elements in the superalloys resulted in the presence of a large number of peaks in the electron spectra, some of which were not fully resolved from each other. For example, the Cr 2s, Al 2p, and Ni 3p peaks overlapped significantly, as did the Mo 3d, Ta 4d, and S 2s peaks, and likewise the Ta 4f, Na 2p, and O 2s. For most of the elements of interest, the intensity data were obtained from other peaks not involved in such overlaps. This necessitated the use of peaks at widely different kinetic energies, which also contributed to the uncertainty (due to the very approximate treatment of λ as a function of E and the neglect of surface contamination effects). The peaks used were: 2p_{3/2} for Ni, Co, Cr, and Ti; 3d_{5/2} for Mo and Nb; 4f_{7/2,5/2} for Ta and W; 2s for Al; 2p_{3/2,1/2} for Cl and S; 1s for C, O, and Na.

When a complex system such as a superalloy is studied by means of ESCA, it is helpful to know the binding energy, shape and satellite structure of the peaks that are expected to appear in the spectral

regions to be examined. This requires knowledge not only of the spectra of pure metals, but also of other oxidation states and chemical environments with which the metals might be associated. Although there is existing literature on the spectra of these metals and many of their compounds (refs. 11 through 19), we chose to obtain our own set of spectra for the superalloy elements as pure metals, as oxidized pure metals, and in a few cases as powdered salts. These data, supplemented with information from the above cited literature, were used as a guide for data analysis (curve resolution and oxidation state identification) of the superalloy spectra.

RESULTS AND DISCUSSION

Surface Composition of "Unoxidized" Superalloy Samples

Samples of B-1900, NASA-TRW VIA, 713C, and IN-738 were examined "unoxidized" (samples machined to size, then cleaned in detergent, acetone, and alcohol) as well as after various periods of high-temperature oxidation at two different temperatures. In Table I the bulk composition of each superalloy is given (ref. 20), along with the average surface composition as computed from the relative intensities of ESCA lines from "unoxidized" unsputtered samples. These data indicate that in each case the surface layer was enriched (relative to the bulk) in Al, Cr, Mo, and Ta; and depleted in Ni by roughly a factor of 2. The surface concentrations of the remaining elements, including Ti, were not markedly different from the bulk values.

In general, the binding energies measured for each element in the unoxidized, unsputtered samples suggested the presence of one or more of the higher oxidation states of the element. The following species were indicated in particular: Ni(II,III)· Cr(III); Al(III); Ti(IV); Co(II,III); Mo(VI); W(VI); Ta(V); and Nb(V). Only for Ni was the metallic (zero-valent) species also observed. However, after 5-10 minutes of sputtering, Ni was found to be solely in the metallic state (fig. 1), and Co was mostly in the metallic state (fig. 2). There was also some evidence of lower oxidation states of Mo, W, Ta, and Nb, while Cr, Al, and Ti were not reduced at all. These seem to be chemical effects of sputtering, and are in general agreement with the observations of Kim and Winograd (ref. 11). In addition, sputtering was often accompanied by a significant decrease in the Mo concentration at the surface. This may be due to the relatively high volatility of MoO_3 at elevated temperatures.

Surface Composition of Oxidized Superalloy Samples

After undergoing oxidation in slowly flowing O_2 at 900 or 1000°C for periods ranging from 0.5 to 100 hours, samples of the four superalloys were found to have generally the same oxidation states represented in the observable surface layer as the "unoxidized" samples had.

Metallic Ni was no longer observed prior to sputtering, however.

Before discussing the observed surface composition of the oxidized superalloys, it is helpful to note that such alloys are generally divided into two groups, depending on the nature of the oxide scale

(refs. 21 & 22). One group, called "alumina formers", typically has a thin continuous surface layer rich in Al_2O_3 adjacent to the metal substrate. In some cases other oxides are dissolved in the alumina or form an external layer over it. The second group, called "chromia formers", has a layer composed primarily of Cr_2O_3 which is underlaid by "tentacles" of Al_2O_3 extending into the metal. Other oxides may dissolve in or form thin layers above or below the Cr_2O_3 . While the concept of these two categories is useful, there are also significant differences among members of each group (depending on the exact alloy composition and oxidation treatment) and even the surface of a single sample may have significant lateral inhomogeneity.

The semi-quantitative ESCA results for oxidized superalloy samples revealed some interesting trends in the average concentration of the alloy elements in the surface layer. These results are presented numerically in Tables II-V and some of the results are illustrated in Figure 3.

On the basis of the ESCA results alone, it can be concluded that B-1900 and NASA-TRW VIA are alumina formers when oxidized at 900 or 1000°C in slowly flowing O_2 . Changes in B-1900 surface composition with oxidation time were generally minor, although the Ti and Cr concentrations increased. Ti and Al increased while Ni and Mo decreased with oxidation time on the NASA-TRW VIA sample surfaces. The surface composition of 713C oxidized at 900°C was found to change dramatically as a function of oxidation time, seeming to fit the alumina-former category after one hour but changing to the

chromia-former category after longer periods of oxidation.

The ESCA results also show that Ti was about an order of magnitude more abundant at the surface of each superalloy after high temperature oxidation than it is in the bulk. TiO_2 was the predominant surface species on IN-738 and the second-most abundant on 713C. In IN-738, Ti constituted 60% of the alloy component abundance in the observed surface layer after just one hour at 900°C . By contrast, the surface concentration of Ti did not exceed the bulk values (1-4%) for any of the "unoxidized" samples, which oxide scale formed at relatively low temperatures during machining (fig. 4). Bourhis and St. John (ref. 32) noted the presence of a TiO_2 layer over the Cr_2O_3 -rich oxide scale on IN-738 and two other superalloys with similar bulk concentrations of Ti. It seems appropriate to designate these as TiO_2 -overlaid chromia formers.

Ni, Cr, Al, and Ti were the only alloy elements that attained a relative surface abundance of more than 10% in any of the samples oxidized at 900 or 1000°C . The surface was depleted in Co (relative to the bulk) in all the Co-containing oxidized samples except for VIA oxidized at 1000°C .

The ESCA results are generally in good agreement with earlier work of some of the authors (ref. 23) who analyzed similar samples by several other methods. An exception occurred for 713C oxidized at 1000°C : the surface abundance of Ni determined by ESCA was only 13%, while Fryburg, et. al., identified by x-ray diffraction a thin black scale

to be mostly NiO. This scale had a marked tendency to spall from samples oxidized for 100 hours. However, the sample analyzed by ESCA (which were oxidized for shorter periods) showed no visible evidence of spallation. Thus, the observed differences could be due to the different oxidation times.

Surface Composition of B-1900 at Successive Stages of Na₂SO₄-Induced Hot Corrosion

Hot corrosion is a complex process of enhanced or catastrophic oxidation known to affect superalloys that are exposed to hot combustion gases, as in gas turbine engine applications. A corrosive deposit forms: molten Na₂SO₄ is widely considered to be its most important constituent (ref. 24).

There is some evidence that hot corrosion in practical systems occurs in two stages (ref. 25): an incubation or induction period, followed by the sudden onset of enhanced or catastrophic oxidation. Fryburg, Kohl, and Stearns (ref. 26) observed such a pattern for the hot corrosion of B-1900, NASA-TRW VIA, 713C and IN-738, using the same reaction conditions employed in this study. B-1900 was found to be the least resistant to this type of attack, having an induction period of about five hours at 900°C, though it is the most resistant to oxidation in the absence of Na₂SO₄.

Figure 5 is a plot of weight-gain versus time for the B-1900 sample that received the longest simulated hot-corrosion treatment prior to analysis by ESCA. The magnitude of the hot corrosion effect is

illustrated by the following comparison: the total weight gained in 29 hours of hot corrosion was nearly 80 mg/cm² (fig. 5) whereas the corresponding gain for simple oxidation (in the absence of Na₂SO₄) was less than 0.2 mg/cm² (ref. 27). Upon cooling, a scale roughly 1 mm thick peeled off in large sections from the sample that was corroded for 29 hours.

The existence of an induction period followed by a sudden acceleration of the oxidation rate is also manifested in Figure 5. The induction period is a time in which little or no weight gain is observed. The length of the induction period is a function of temperature, alloy composition, amount of Na₂SO₄, and preoxidation of the sample. In addition, it is difficult to define the length in a relevant quantitative way. We have arbitrarily chosen the period of time required for the specimens to attain a specific weight gain of 0.3 mg/cm². For the conditions illustrated in Figure 5, the data indicate an induction period of five hours.

In this ESCA study, we sought to elucidate the reaction mechanisms by which the normally protective oxide scale of B-1900 is destroyed, by observing changes in surface composition during the first few hours of simulated hot corrosion.

Na₂SO₄ Coating

To test the effectiveness of the application of Na₂SO₄, a B-1900 sample was analyzed after being preoxidized, then coated to a Na₂SO₄ coverage of 3 mg/cm². The ESCA spectra showed no distinct peaks for

the alloy elements, indicating that the coverage was complete. The spectra for Na, S, and O were in agreement, in terms of binding energy and relative intensity, with those for Na_2SO_4 powder (which was mounted on double-sided tape for examination by ESCA). There was one exception to this agreement: the Na intensity was greater than the stoichiometric value by a factor of 1.5 for the Na_2SO_4 -coated sample. Also, the presence of Cl on the coated samples, at a concentration 2-3% as great as Na, was established. The source of the Cl contamination was not apparent. The concentration of Cl was less than 10 ppm in the Na_2SO_4 (before application) and in the water used in the application of the Na_2SO_4 .

Hot Corrosion for 5-45 Minutes (Early Induction Period)

Four experiments were carried out to determine the effect of very short periods of exposure to hot corrosion conditions. The preoxidized sample discussed above was washed, recoated with Na_2SO_4 (3 mg/cm^2), then heated to 900°C for 5 minutes in one atmosphere of slowly flowing O_2 . The ESCA analysis of this sample showed mainly Na_2SO_4 , in the expected stoichiometry, but also showed small amounts of Ni, Cr, and possibly Al. The abundance of each of these elements relative to Na was probably less than 2%. Cl was again present at the 3% level relative to Na.

The same sample was later subjected to an additional 30 minutes of hot corrosion treatment, another sample was given a similar 30-minute treatment, and an unoxidized sample was coated with 0.6 mg/cm^2 of

Na_2SO_4 and corroded for 45 minutes. The ESCA analysis of each of these samples showed clearly that all the alloy elements were present in the observable surface layer. Al and Cr were, respectively, the most and next-most abundant alloy elements in the first and third samples, while the order was reversed for the second sample. The total alloy metal abundance (relative to Na) ranged from 0.3 to 0.8 for these samples. This is an important observation, indicating that the transfer of significant amounts of material from the oxide layer to the surface of the salt layer begins early in the induction period, long before the onset of rapidly accelerating weight-gain. The analyses of these three samples also showed a consistently low ratio of S to Na, ranging from 0.22 to 0.29.

Hot Corrosion for 2-8 Hours (Induction Period and Early Acceleration)

Eight preoxidized, Na_2SO_4 -coated (3 mg/cm^2), B-1900 samples were prepared, and subjected (two samples for each treatment) to hot corrosion for 2, 4, 6, and 8 hours. The average surface compositions determined by semi-quantitative ESCA are illustrated in Figures 6, 7, and 8.

Figure 6 shows elemental abundances relative to Na for most of the alloy elements and for S and Cl. The results for the 2 and 4 hour treatments support the conclusion that a significant amount of material from the oxide layer reaches the surface of the salt layer during the induction period.

The atomic abundance of S (identified via ESCA binding energies as

$\text{SO}_4^{=}$) relative to that of Na is rather close to the stoichiometric value for Na_2SO_4 (0.5) after 2, 4, and 6 hours of corrosion. However, the relative S abundance decreased by a factor of 10 for the samples corroded for 8 hours. Such a decrease in $\text{SO}_4^{=}$ at the end of the induction period was also observed previously (ref. 26), by washing similarly-corroded B-1900 samples in water and analyzing the elements thus extracted.

The observation that all the alloy elements are much less abundant relative to Na in the 6 and 8 hour samples than in the 2 and 4 hour samples is a phenomenon that remains to be explained. If one assumes that the alloy elements detected by ESCA are soluble components of the molten Na_2SO_4 , the decrease in relative abundance could be explained by a reconversion to the appropriate oxide and subsequent precipitation. This would agree with the layered oxide structure often observed on hot corrosion samples, and would also agree with a similar decrease in soluble aluminum and chromium observed at the end of the induction period by Fryburg, Kohl, and Stearns, using similarly corroded B-1900 samples. Further work would be required to elucidate this point.

Figure 7 shows the average alloy element concentrations (for the same samples) computed by setting the total abundance of the seven metals of the alloy equal to 100%. The composition changes which occur among the alloy elements over the 2 to 6 hour period of time seem to be rather minor. A rough similarity to the surface composition of B-1900 oxidized in the absence of Na_2SO_4 may be noted. The increase in Al

and Ni and decrease in other alloy elements at the surface of the 8 hour samples may be significant because the corrosion rate has begun to accelerate by that time.

Figure 8 illustrates the results obtained from analyses of the same samples after they were washed in distilled water (to remove the Na_2SO_4 and other water-soluble phases) and oven-dried. While the washing procedure changed the macroscopic appearance of the samples significantly, the general pattern of the alloy element abundances remained much the same. Ni and Co were somewhat more abundant after washing in the 2 and 4 hour samples. The prevalence of Al in the 6 and 8 hour samples was also increased after washing. Cl was present on the washed samples at 3-7% abundance relative to the total alloy element abundance.

The core level binding energies (E_b) observed for corroded B-1900 samples have been employed to identify oxidation states and, for some elements, specific chemical species that are present at the surface. The ESCA spectra of Na_2SO_4 , Al_2O_3 , NaAlO_2 , $\text{Al}_2(\text{SO}_4)_3$, $\text{NaAl}(\text{SO}_4)_2$, and Na_2CrO_4 powders were recorded to facilitate the interpretation of binding energy results for the corroded samples. There is some inherent uncertainty in the comparison of measurements made on tape-mounted powders with those made on other types of surfaces; however, the E_b values for Na_2SO_4 powder were found to agree within experimental error (± 0.3 eV) with those for Na_2SO_4 -coated B-1900 samples (both before and after a 5-minute heat treatment at 900°C).

The average Al 2s binding energy for the corroded samples was 119.3 eV which indicates that Al_2O_3 is the predominant Al species. The Al 2s E_b of NaAlO_2 is only 0.3 eV lower than that of Al_2O_3 ; thus, the presence of some NaAlO_2 can be neither firmly established nor ruled out. The observation of NaAlO_2 would constitute evidence for the "basic fluxing" model of hot corrosion (ref. 28), in which the Na_2SO_4 layer becomes enriched in O^{2-} and dissolves Al_2O_3 as AlO_2^- .

Conversely, the detection of Al^{3+} that is not directly bonded to oxygen would constitute evidence for the "acidic fluxing" model of hot corrosion (ref. 28), in which Al_2O_3 dissolves as Al^{3+} because of O^{2-} deficiency in the molten Na_2SO_4 layer. The detection of such Al^{3+} species by ESCA seems feasible because $\text{Al}_2(\text{SO}_4)_3$ and $\text{NaAl}(\text{SO}_4)_2$ were found to have rather large Al 2s binding energy shifts (1.3 eV and 1.4 eV, respectively) relative to Al_2O_3 . A small "high E_b shoulder" was observed in the Al 2s spectra of several corroded samples; however, a careful review of the Al 2s and Al 2p spectra showed that no significant amount of the observed Al could be identified as Al^{3+} in an $\text{Al}_2(\text{SO}_4)_3^-$ or $\text{NaAl}(\text{SO}_4)_2^-$ -like environment.

In both the acidic and basic fluxing models, a stoichiometry gradient is presumed to exist across the salt layer, such that the Al^{3+} or AlO_2^- ions formed at the salt/alloy interface would be likely to reform as Al_2O_3 at the salt/atmosphere interface. This suggests that the search for Al^{3+} or AlO_2 should be continued toward the salt/alloy interface. Mechanical removal of peripheral layers, followed by ESCA analysis, is a possible approach.

On the basis of Cr $2p_{3/2}$ binding energies and peak shapes, the corroded samples were found to have both Cr(VI) and Cr(III) present in the surface layer. Cr(VI) accounted for 50-80% of the Cr intensity and, because some reduction of Cr(VI) occurred during ESCA runs, it can be concluded that Cr(VI) is generally predominant at the surface. The ratio of Cr(VI) to Cr(III) was significantly greater after 6 hours of corrosion than at 4 hours (see fig. 9). The average Cr(VI) binding energy of 579.3 eV for corroded samples is within experimental error of that observed for Na_2CrO_4 powder (579.5) as well as the most recent literature value for CrO_3 (579.07) (ref. 13). Na_2CrO_4 and Na_2SO_4 are not clearly distinguishable on the basis of Na 1s binding energies. The pale yellow color observed on some corroded samples is indicative of Na_2CrO_4 , however.

For Ni, Co, Mo, Ta, and Ti the same oxidation state(s) that was identified for B-1900 oxidized in the absence of Na_2SO_4 seemed to be present on the surface of the corroded samples.

Hot Corrosion for 15-29 Hours (Extensive Attack)

Two preoxidized B-1900 samples were coated with Na_2SO_4 (3 mg/cm^2) and heated for 15 and 29 hours respectively, at 900°C in slowly flowing O_2 . The 15 hour sample exhibited extensive corrosion over the entire surface, but remained intact so the surface could be examined by using ESCA. The alloy elements were found to be significantly more abundant relative to Na in this sample than in any previous corroded sample: Ni which accounts for 35% of the total alloy elements

observed, is nearly as abundant as Na. The other elements contributing more than 10% of the alloy component total are Al(31%) and Ti(12%). This sample has a surface composition intermediate between those of the Al_2O_3 -dominated samples (2-8 hour corrosion) discussed above, and the NiO-dominated ones (up to 100 hour corrosion) which Stearns, Kohl, and Fryburg (ref. 30) examined by x-ray diffraction.

The S 2p peak is barely detectable for the 15 hour sample, S being less than 2% as abundant as Na, and about the same as Cl.

The binding energies of Cr, Co and Al are significantly lower than for previous corroded samples, indicating different oxidation states or chemical environments. Most of the Cr was found to be in the Cr(III) oxidation state. The Co $2p_{3/2}$ binding energy, width, and shakeup structure are in agreement with recent results for CoO (ref. 31). The E_b for Al 2s is 118.5 eV, or 0.8 eV below Al_2O_3 and 0.5 eV below NaAlO_2 : the chemical environment of Al remains to be identified.

The sample corroded for 15 hours was subsequently washed in water; however, a scale a few tenths of a millimeter thick began to peel off during the process. The sample was again analyzed by ESCA after the scale had been carefully removed. The surface composition, considering alloy elements only, was found to be: Ni, 42%; Al, 16%; Mo, 16%; Co, 12%; Cr, 9%; Ta, 4%; and Ti, 2%.

A scale roughly 1 mm thick detached itself in large pieces from the surface of the 29 hour sample upon cooling after the hot corrosion

treatment. This provided an opportunity to examine the interface where spontaneous scale separation occurs. The surface of the oxide that was retained on the sample was found to consist primarily of Mo and Ni. The ESCA results indicate the following composition, considering alloy components only: Mo, 39%; Ni 33%; Al, 11%; Cr, 7%; Co, 6%; Ta, 2%; and Ti, 1%. This provides evidence in support of the conclusions reached by Stearns, Kohl, and Fryburg (ref. 30) on the basis of x-ray diffraction analysis of similar samples: the most prominent phase is NiMoO_4 which probably contains a considerable fraction of CoMoO_4 and is accompanied by a phase of mixed Al-Cr spinel. The relative abundances from the ESCA results substantiate the $(\text{Ni,Co})\text{MoO}_4$ stoichiometry: the ratio of Ni + Co to Mo is 1.0, while the ratio of O to Mo is 4.1. Bourhis and St. John (ref. 32) also identified NiMoO_4 at a somewhat similar spalling interface.

SUMMARY AND CONCLUSIONS

This work clearly demonstrates the usefulness of ESCA in the study of oxidation and corrosion of superalloys (and other complex materials) in spite of its semiquantitative nature. We will emphasize seven principal conclusions of this work:

1. The surface of each of the "unoxidized" superalloy samples (which were machined to shape and cleaned with detergent, acetone, and alcohol prior to examination) was found to be significantly enriched in Al and Cr relative to the bulk. In each case, the percentage enrichment of Al exceeded that of Cr.

2. ESCA results for samples oxidized at 900 or 1000°C in slowly flowing O₂ showed clearly that B-1900 and NASA-TRW VIA are alumina formers and that the surface of IN-738 is primarily TiO₂. However, the surface composition of 713C oxidized at 900°C was found to change dramatically as a function of oxidation time, seeming to fit the alumina-former category after one hour but changing to the chromia-former category after longer periods of oxidation.
3. The surface of all the superalloy samples oxidized at high temperature was greatly enriched in Ti relative to the bulk. TiO₂ is the predominant surface phase on oxidized IN-738 and the second-most abundant on 713C. By contrast, the surface concentration of Ti did not exceed the bulk values (1-4%) for any of the "unoxidized" samples.
4. For preoxidized B-1900 samples exposed to just 30-45 minutes of Na₂SO₄-induced hot corrosion, the total alloy element abundance at the surface ranged from 0.3 to 0.8 relative to Na. Thus, the transfer of significant amount of material from the oxide layer to the surface of the salt layer begins long before the onset of rapidly accelerating weight-gain. A decrease in total alloy element abundance relative to Na was, however, observed after 6 hours of hot corrosion.
5. The ratio of Cr(VI) to Cr(III) was significantly greater after 6 hours of corrosion than at 4 hours. The atomic abundance of S relative to Na at the surface of Na₂SO₄-coated B-1900 samples decreased an order of magnitude, from 0.43 after 6 hours of hot corrosion to 0.04 after 8 hours. Among the alloy elements, Al and Ni

increased in relative surface abundance and all the others decreased over the 6 to 8 hour period. Thermogravimetry showed that the onset of rapidly accelerating oxidation took place during this period.

6. For a B-1900 sample examined after 15 hours of Na_2SO_4 -induced hot corrosion, the surface abundances of Na, Ni, and Al were roughly equal, with Ni and Al accounting for two-thirds of the alloy element abundance. The oxide scale which remained attached after spontaneous spallation from a sample corroded for 29 hours was found to consist primarily of Mo and Ni. The spallation interface seems on the basis of stoichiometry, to be mostly $(\text{Ni},\text{Co})\text{MoO}_4$.

7. ESCA binding energies were interpreted to identify the chemical state of the alloy elements in oxidized and corroded samples. The results did not enable a distinction between the previously proposed mechanisms of Na_2SO_4 -induced hot corrosion.

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TABLE I

BULK^a AND SURFACE^b COMPOSITION OF "UNOXIDIZED" SUPERALLOYS

Element	Alloy							
	B-1900		NASA-TRW VIA		Alloy 713C		IN-738	
	Composition, Atom Percent Metal							
	Bulk	Surface	Bulk	Surface	Bulk	Surface	Bulk	Surface
Ni	62.5	31	64.5	28	67	39	59	32
Cr	8.7	17	7.1	9	13.2	24	17.5	30
Al	12.6	30	12.2	40	12.4	31	7.2	22
Ti	1.2	1	1.3	0.7	0.9	0.5	4.0	4
Co	9.6	11	7.7	3	-	-	8.2	6
Mo	3.5	7	1.3	13	2.4	4	1.0	4
W	-	-	1.8	2	-	-	0.8	-
Ta	1.4	3	3.0	5	-	-	0.6	1
Nb	-	-	0.3	-	1.2	2	0.6	0.8
Other	0.5	-	0.8	-	3.0	-	0.9	-

^a Adapted from Fryburg, Miller, Kohl, and Stearns (Ref. 20)^b From semiquantitative treatment of ESCA data.

TABLE II

Surface Composition of Oxidized B-1900

Atomic % (Alloy Elements Only)

<u>Oxidation Time (Temp)</u>	<u>0.5 Hr (900°C)</u>	<u>2 Hr (900°C)</u>	<u>70 Hr (900°C)</u>	<u>100 Hr (1000°C)</u>
<u>Element</u>				
Ni	10	7	8	7
Cr	4	3	14	5
Al	69	75	53	68
Ti	4	4	11	8
Co	6	6	6	5
Mo	7	5	6	3
Ta	.9	-	.8	2
Zr	-	.1	.4	.3
Hf	-	.1	.2	2

TABLE III

Surface Composition of Oxidized NASA-TRW VIAAtomic % (Alloy Elements Only)

<u>Oxidation Time</u> <u>(Temp)</u>	<u>0.5 Hr</u> <u>(900°C)</u>	<u>24 Hr</u> <u>(900°C)</u>	<u>100 Hr</u> <u>(900°C) ^a</u>	<u>100 Hr</u> <u>(900°C) ^a</u>	<u>100 Hr</u> <u>(1000°C)</u>
<u>Element</u>					
Ni	35	21	12	15	12
Cr	13	12	14	16	11
Al	38	52	53	47	52
Ti	5	11	17	14	9
Co	3	2	2	5	7
Mo	4	2	.9	.7	1
W	1	.5	1	.8	3
Ta	.7	.2	.1	.6	2
Hf					1
Nb					.5
Zr					1

^aResults for two different samples given the same treatment

TABLE IV

Surface Composition of Oxidized Alloy 713C

Atomic % (Alloy Elements Only)

<u>Oxidation Time (Temp)</u>	<u>1 Hr (900°C)</u>	<u>19 Hr (900°C)</u>	<u>64 Hr (900°C)</u>	<u>50 Hr (1000°C)</u>
<u>Element</u>				
Ni	5	14	15	13
Cr	8	32	40	30
Al	78	25	16	27
Ti	3	23	23	22
Mo	5	4	4	5
Nb	1	2	2	3

TABLE V

Surface Composition of Oxidized IN-738Atomic % (Alloy Elements Only)

<u>Oxidation Time (Temp)</u>	<u>1 Hr (900°C)</u>	<u>22 Hr (900°C)</u>	<u>100 Hr (900°C)</u>	<u>43 Hr (1000°C)</u>
<u>Element</u>				
Ni	2	3	5	<4
Cr	27	33	26	33
Al	5	3	7	<3
Ti	60	58	58	57
Co	.9	1	3	3
Mo	3	1	.8	<.1
Ta	1	.9	.7	<.1
Nb	.3	.2	.2	.3

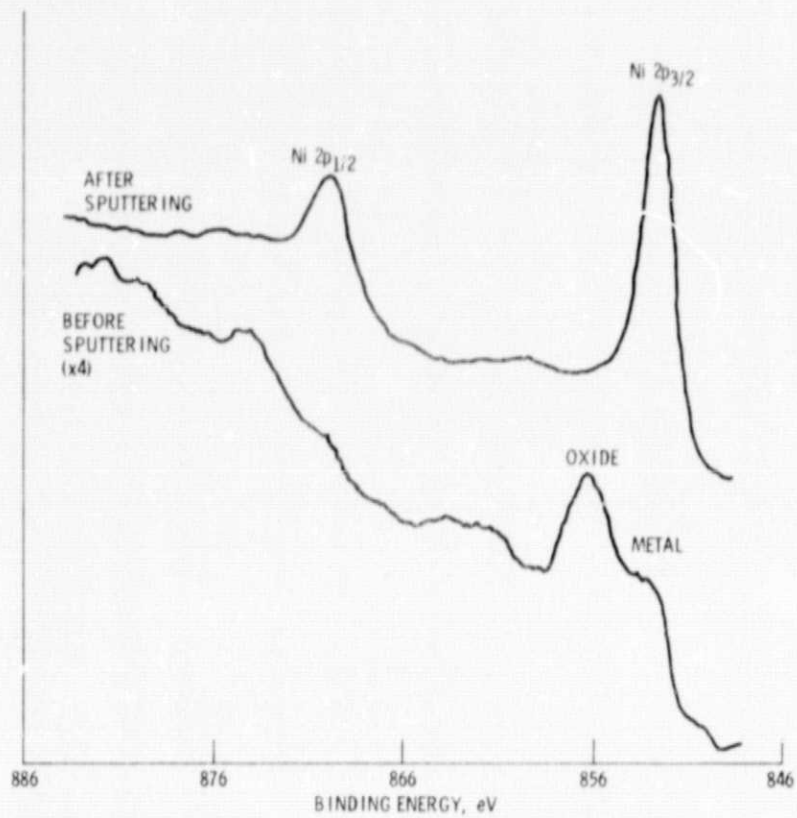


Fig. 1. Comparison of Ni 2p photoelectron lines recorded before and after Ar ion sputtering of an unoxidized NASA-TRW VIA sample.

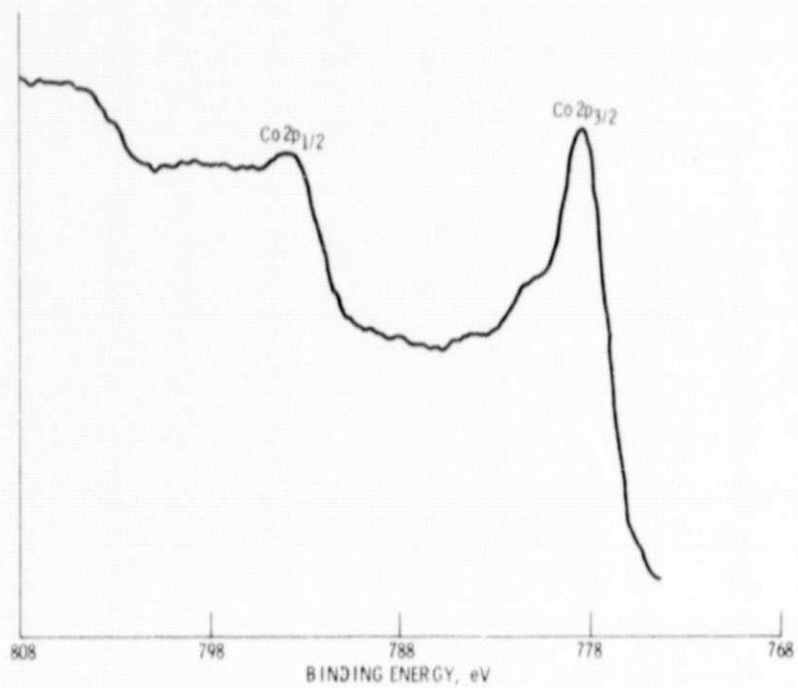


Fig. 2. A Co 2p photoelectron spectrum, recorded after Ar ion sputtering of an unoxidized NASA-TRW VIA sample, showing Co mostly in the metallic state.

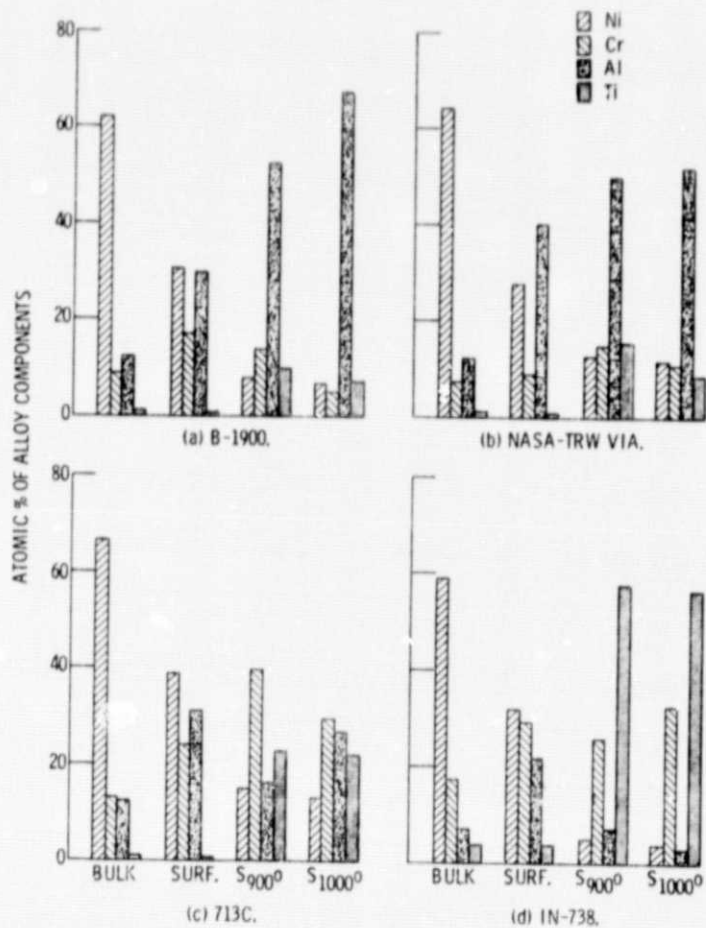


Fig. 3. Comparison of the bulk and surface abundances of Ni, Cr, Al, and Ti in superalloys: a) B-1900, b) NASA-TRW VIA, c) 713C and d) IN-738. "Bulk" and "Surface" data are from chemical and ESCA analyses, respectively, of unoxidized alloy samples. "S900°" and "S1000°" data are from ESCA analyses of samples oxidized for 100 hours at 900 and 1000°C, respectively. The total observed abundance of the alloy components (Ni, Cr, Al, Ti, Co, Mo, Ta, Hf, and Zr) was taken as 100% in each case.

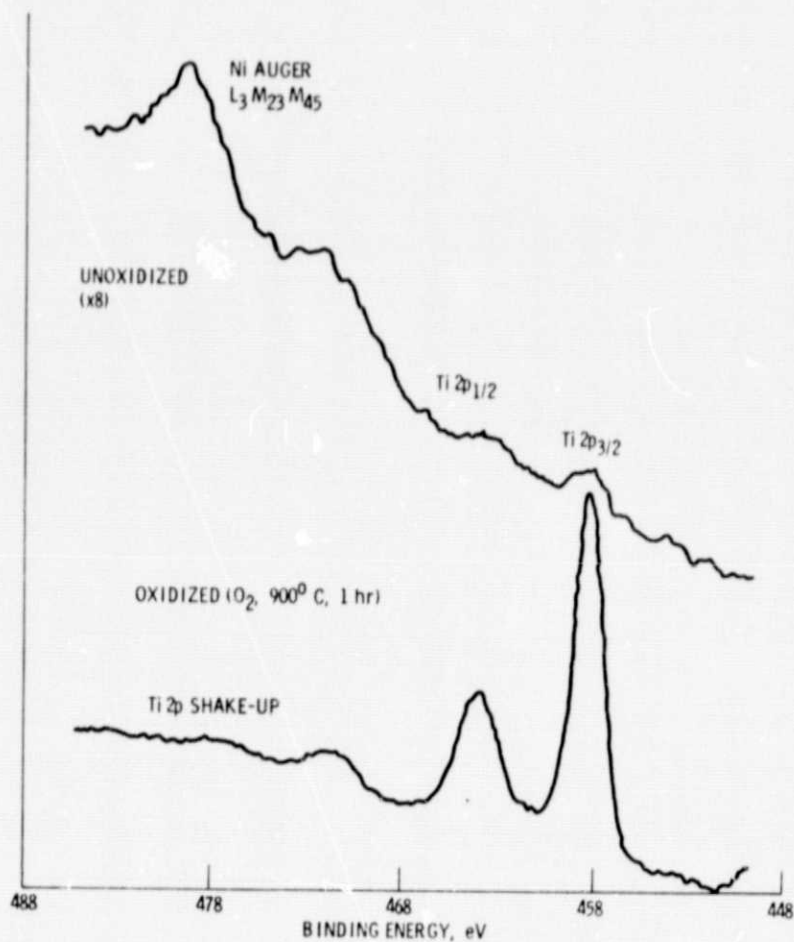


Fig. 4. Comparison of Ti 2p photoelectron lines from unoxidized and oxidized IN-738 samples, illustrating the marked Ti enrichment of the surface that accompanies high temperature oxidation. A concurrent decrease in Ni is evident from the x-ray induced Auger peaks.

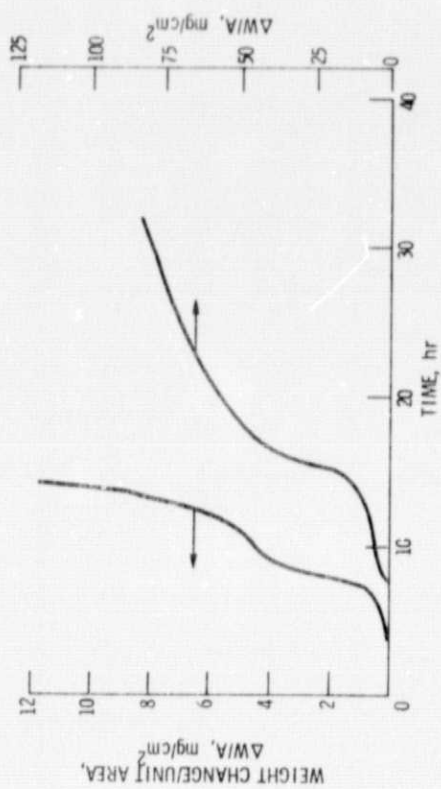


Fig. 5. Rate of hot corrosion of B-1900 at 900°C in 1 atmosphere of slowly flowing oxygen. (Sample preoxidized for 100 hours at 900°C) Na_2SO_4 dosage, 3 mg/cm².

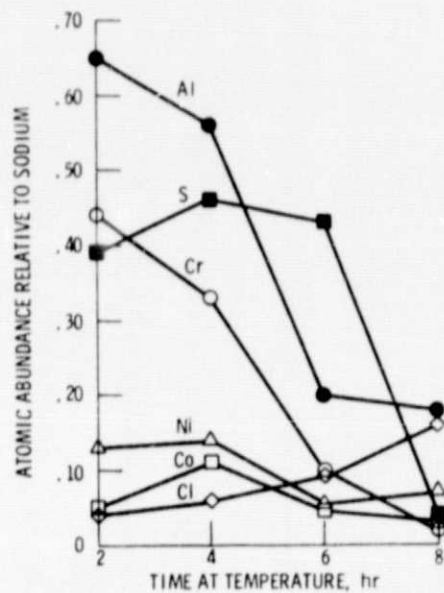


Fig. 6. Approximate surface composition of B-1900 during the early stages of Na_2SO_4 -induced hot corrosion at 900°C . (Other elements observed, but not included in this graph, were C, O, Ti, Mo, and Ta.)

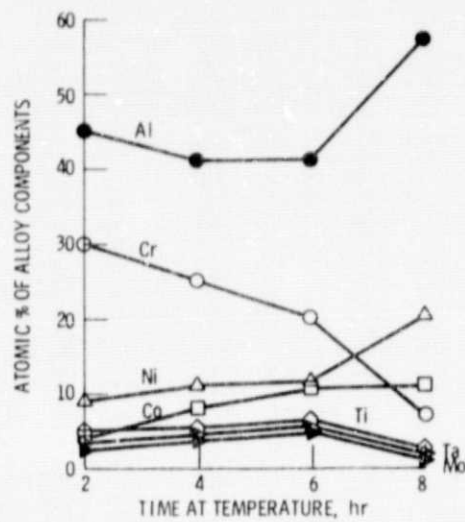


Fig. 7. Approximate relative abundance of alloy components at the surface of B-1900 during the early stages of Na_2SO_4 -induced hot corrosion at 900°C . (Total abundance of alloy components is taken as 100%.)

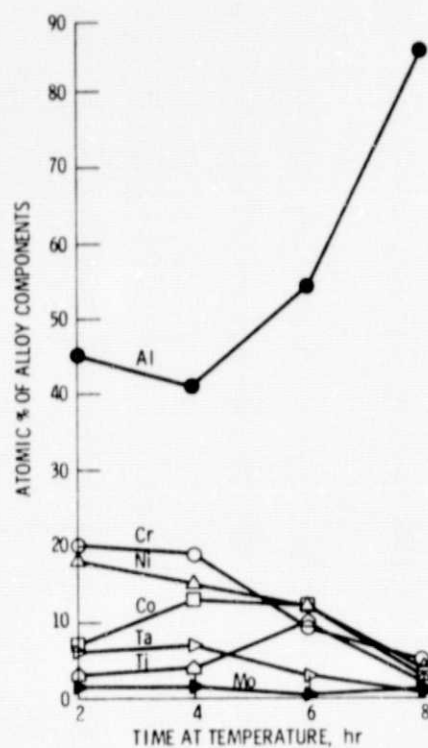


Fig. 8. Approximate relative abundance of alloy components at the surface of hot corroded (900°C) B-1900 samples after washing. (Total abundance of alloy components is taken at 100%.)

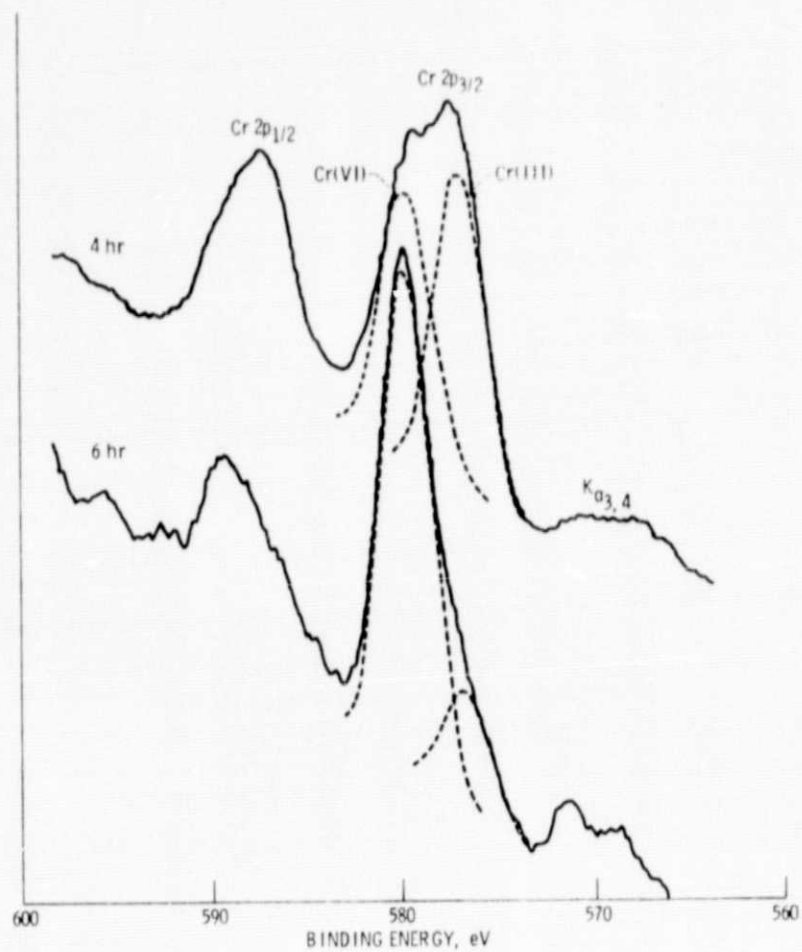


Fig. 9. Cr 2p photoelectron spectra from B-1900 samples after 4 and 6 hr of Na₂SO₄-induced hot corrosion. Cr(VI) and Cr(III) contributions within the Cr 2p_{3/2} peaks are resolved.

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15. Supplementary Notes Final report. Project Manager, Fred J. Kohl, Materials and Structures Division, NASA Lewis Research Center, Cleveland, Ohio 44135. Appendix I - ESCA Study of Oxidation and Hot Corrosion of Nickel-Base Superalloys by Steven R. Smith, William J. Carter III, and Gheorghe D. Mateescu, Case Western Reserve University, and Fred J. Kohl, George C. Fryburg, and Carl A. Stearns, NASA Lewis Research Center.					
16. Abstract <p>A study of the high temperature oxidation and Na_2SO_4-induced hot corrosion of some nickel-base superalloys has been accomplished by using ESCA to determine the surface composition of the oxidized or corroded samples. Oxidation was carried out at 900° or 1000° C in slowly flowing O_2 for samples of B-1900, NASA-TRW VIA, 713C, and IN-738. Oxidation times ranged from 0.5 to 100 hr. Hot corrosion of B-1900 was induced by applying a coating of Na_2SO_4 to pre-oxidized samples, then heating to 900° C in slowly flowing O_2. Corrosion times ranged from 5 min to 29 hr. For oxidized samples, the predominant type of scale formed by each superalloy was readily determined, and a marked surface enrichment of Ti was found in each case. For corroded samples, the transfer of significant amounts of material from the oxide layer to the surface of the salt layer was observed to occur long before the onset of rapidly accelerating weight-gain. Some marked changes in surface composition were observed to coincide with the beginning of accelerating corrosion, the most striking of which were a tenfold decrease in the sulfur to sodium ratio and an increase in the Cr(VI) to Cr(III) ratio.</p>					
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